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ION IMPLANTATION IN PEROVSKITE TYPE FERROELECTRICS.(U)

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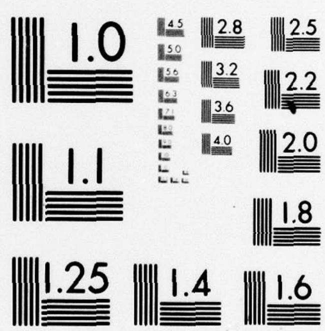


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PROGRESS REPORT NO. 6

FINAL REPORT

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# 6 "ION IMPLANTATION IN PEROVSKITE TYPE FERROELECTRICS".

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UNIVERSITY OF MISSOURI-ROLLA
ROLLA, MO 65401



10 ROBERT GERSON

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## CONTENTS

Activities for the Period June 30, 1979, to October 31, 1979:

Publications: Abstract (attached) submitted to March meeting (Solid State), American Physical Society.

Meeting date: March 24-28, 1980 (New York)

Abstract title: "Depth Profiles of Electrical Conductivity in Implanted Strontium Titanate", Robert Gerson, Edward B. Hale, and Paul Himmelfarb.

Scientific personnel supported by this project:

Post-doctoral: Kazushi Sugawara

Research aide: Claire Yates

Connie M. Cooper, who was supported by the project, but who was unable to remain on the UMR campus because her husband has a position in Minneapolis, has almost finished a dissertation based on measurements she made here.

Degrees granted: None

DAAG 29-77-G-0001

REPORT 6 - FINAL REPORT

## Statement of the Problem

The object of this work was to study ion implantation in perovskite ferroelectrics. In particular it was desired to investigate the conductive behavior of implanted layers. The accelerator used for implantation operates at a maximum voltage of 200 kV, limiting the ion implantation depth to a few hundred nanometers, and thus determining the thickness of the implanted layer.

While it was clear at the beginning of the program that conductive layers could be made, many experimental conditions were unknown. These included the type and magnitude of the attainable conductivity, the type of ion which could most effectively be implanted, and the dose levels required. It was also not clear which ferroelectric would be the best host crystal for the purposes of this study. Many of these questions have been resolved in the course of the work.

## Summary of Important Results

Implantation experiments were conducted on a number of substrate crystals and ceramics: strontium titanate, barium titanate (single crystal and ceramic), titanium dioxide, lithium niobate, and lithium tantalate. A wide variety of ions ($H^+$, $B^+$, $C^+$, $N^+$, $Fe^+$, $Ar^+$, $As^+$, $Ta^+$ and $Nb^{++}$) were used in implantation experiments. The most effective of these ions in producing conductivity was boron. Niobium was also found to be quite effective, but little work was done with this element because ion beams of niobium are difficult to maintain. Iron and chromium were found to be useful, particularly since both of these ions can be detected by spin resonance techniques.

There were two crystals in which significant conductivity was not detected in the implanted layers: barium titanate and lithium tantalate. In the context of these experiments this means that the room temperature sheet resistance of the implanted layers of these crystals was above $10^{10}$ ohms per square, indicating a bulk resistivity in the implanted layer above $10^{5}$ ohm cm. On the other hand implanted ceramics of barium titanate did become conductive, and showed some of the features of conductivity in strontium titanate. The marked positive temperature coefficient anomalies often observed in bulk semiconducting barium titanate near the Curie point was not found in these implanted layers. These anomalies in the bulk ceramic have been attributed to grain boundary electronic effects which are apparently suppressed in the implanted layer.

<u>Strontium Titanate</u>

The most heavily investigated system was boron *implanted* in strontium titanate. A wide range of semiconductors and semimetals was produced with sheet resistances at room temperature from 100 to 100,000 ohm/square, corresponding to volume resistivities from $10^{-3}$ to 1 ohm cm in the implanted layer. These materials were n-type semiconductors with Hall mobilities of about 5 $cm^2$/volt sec at room temperature and 100 $cm^2$/volt sec at 77 K. They were produced by implantation doses in the range of $10^{16}$ to $10^{17}$ ions/$cm^2$, followed by a thermal treatment (annealing) at 200 to 300 C. The donor responsible for the conductivity appears to be boron in association with a lattice imperfection. The nature of the imperfection is still unknown.

The implanted layers show the usual phenomena associated with semiconductors made from strontium titante, such as a high Seebeck coefficient, 100 to 300 millivolt/degree K. We also measured diode characteristics when

the layers were contacted by metals. There was a limit to the type of experiments possible because the implanted layers are only about 500 nm thick, and no way is known to make similar boron-doped semiconductors in bulk strontium titanate.

The conductivity annealing of strontium titanate implanted with boron is a process which, in spite of considerable experimental study, we understand only at a macroscopic rather than at a microscopic level. Immediately after implantation the boron-containing layers typically have a sheet resistance between $10^6$ and $10^7$ ohms/square, which is stable if the samples are left at room temperature. If the conductivity is measured in a narrow range near room temperature, the samples are found to be semiconducting with an activation energy of a few tenths of an electron volt. Heating the sample to temperatures between 200-300 C for periods of about an hour increases the conductivity and decreases the activation energy. At one stage in the annealing the activation energy becomes zero (semimetallic behavior) and the sheet resistance 100 to 1000 ohms per square. At this maximum conductivity there is about one conducting electron in the layer for ten implanted boron atoms. Continued heating at high temperature again increases the sheet resistance, and the sample is again semiconducting.

Our studies of conductivity, Hall effect, and Seebeck effect have not resolved the nature of the defects which serve as donors. Electron spin resonance studies of the system were not successful. Optical spectroscopy showed only broad absorption bands which are not useful in pinpointing the mechanisms. Recently Drs. Meera and Holalkere Chandrasekhar (University of Missouri-Columbia) have kindly volunteered to attempt Raman measurements on these bombarded layers. The shape and thickness of the layers are ideal for

Raman spectroscopy, and we hope that these studies will yield useful data. The measurements should be helped considerably by our recently developed stripping techniques which can remove the highly damaged outer layer of strontium titanate. This layer is not significantly conductive in the semimetallic range.

The stripping technique discussed above consists of stepwise removal of the implanted layer by phosphoric acid. At a temperature of 55 C the layer removal proceeds over a period of hours, permitting the profiling of resistivity as a function of depth. Our stripping experiments have resulted in two important conclusions:

1) The implantation depth in strontium titanate is two to three times greater than would be predicted by the most simple extension of range theory.

2) The observed conductivity of the implanted layers is deep in the layer, not at the surface. The surface has undergone the heaviest loss of oxygen, and has the lowest residual boron, of any part of the implanted layer. The finding that the conductivity is deep in the implanted layer substantiates the major role of the boron ion in causing the conductivity.

In some implanted strontium titanate crystals a conductivity anomaly was observed at the temperature of a displacive transition (105 K). A conductivity decrease was found in implanted layers at this cubic-tetragonal phase change, but only for layers showing semiconductive characteristics. For the more heavily conductive semimetallic layers this anomaly was not observed. The anomaly has not been reported in bulk conductive strontium titanate. Several models can be used to explain its occurrence in the implanted layer, but the most reasonable explanation is electron scattering by the soft mode, or by local impurity modes which soften at the transition temperature.

## Lithium Niobate

Conductive layers were also found on lithium niobate crystals, implanted with both boron and iron. No increase in conductivity due to annealing was observed in this crystal. For crystals implanted with $10^{17}$ ions/cm$^2$ of boron the room temperature sheet resistance was $2 \times 10^5$ ohms/square, while the same dose of iron ions caused a sheet resistance of about $10^4$ ohms/square. At lower ion doses for both implants the conductivity decreased very rapidly with decreasing dose. All of the implanted layers were semiconducting with activation energies in the 0.1 to 0.2 eV range, except for the sample with $10^{17}$ iron ions/cm$^2$, which was essentially semimetallic.

In spite of the considerable technological importance of lithium niobate crystals little is known of conductivity processes in the material. The only reported mobility measurements were made using photoconductive techniques and resulted in a value of about 1 cm$^2$/volt second at room temperature. Our data were consistent with this value, although the signal/noise ratio was low in our Hall effect measurement and the precision of our result was poor.

We did not succeed in creating layers of measurable conductivity by ion bombardment of lithium tantalate.

## Rutile

Conductive layers were made on rutile crystals by ion implantation with boron. For boron doses of $10^{17}$ ions/cm$^2$ the room temperature sheet resistance was about 5,000 ohm/square. The sheet resistance is temperature dependent, varying from about 1000 ohm/square at 500 K to $10^5$ ohm/square at 125 K. In this temperature range the Hall mobility was found to show unusual behavior, increasing with temperature over most of the range, but decreasing sharply near 300 K. The measured mobility values were between 1 and 8 cm$^2$/volt second.

The magnitude of the mobility is in agreement with values measured for reduced crystalline rutile, but the variation with temperature is completely different. In the bulk crystal the published data show that electron mobility is limited by phonon scattering, while our data suggest that in the implanted layer the primary scattering centers are ionized impurities. Again, some form of surface spectroscopy will be necessary to substantiate these conclusions.

## SUMMARY

A variety of novel layer semiconductors have been formed on the surface of a number of perovskitic or perovskite-like crystals by the implantation of various ions. In particular boron has proved to be surprisingly effective as an implant ion causing conductivity. Iron has also proved useful, especially since it can be studied by electron spin resonance after implantation. Recently developed techniques for chemical stripping of the implanted layer will permit a better evaluation of the interactions of implant ions and other imperfections. Progress in understanding should lead to device applications of these novel materials.

Papers Published

"Conductive Strontium Titanate Layers Produced by Boron-Ion Implantation", Connie M. Cooper, P. S. Nayar, Edward B. Hale, and Robert Gerson, J. Appl. Phys. 50, 2826 (1979).

"Electrical Properties of Strontium Titanate Crystals Implanted with Boron", Robert Gerson, C. M. Cooper, P. S. Nayar, and E. B. Hale, Bull. Amer. Phys. Soc. 23, 367 (1978).

"Electrical Properties of Lithium Niobate Crystals Implanted with Boron", Robert Gerson, P. S. Nayar, C. M. Cooper, and E. B. Hale, Bull. Amer. Phys. Soc. 24, 507 (1979).

"Electrical Conductivity in Ion Implanted $SrTiO_3$", K. Sugawara, E. B. Hale, and R. Gerson, to be published in conference proceedings, Materials Research Society, Annual Meeting, 1979 (Boston).

"Depth Profiles of Electrical Conductivity in Implanted Strontium Titanate", Robert Gerson, Edward B. Hale, and Paul Himmelfarb, to be published, Bull. Amer. Phys. Soc., 1979.

Personnel Supported:

During the period of the grant Robert Gerson was principal investigator and received summer salary.

Nov. 1, 1976 - June 30, 1977:

The grant was the principal source of support to:

Henry Glotfelty: postdoctoral appointment
Connie M. Cooper: graduate student

Partial or summer support was also given to the following students:

Daniel H. Perkins
Claire Y. Guidicini
Jeffrey B. Johnson

July 1, 1977 - December 31, 1977:

Post-doctoral: Parameswaram S. Nayar
Graduate Student: Connie M. Cooper

In addition partial or summer support was extended to the following:

Carolyn Krebs, Claire Yates, Jeffrey B. Johnson, Samar Sinharoy, Daniel H. Perkins

Jan. 1, 1978 - June 30, 1978:

Post-doctoral: Parameswaram S. Nayar
Graduate Student: Connie M. Cooper

July 1, 1978 - Dec. 31, 1978:

Post-doctoral: Parameswaram S. Nayar (until Oct. 31, 1978)
Graduate Student: Connie M. Cooper (until Sept. 30, 1978)
Research Aide: Claire Yates (from Oct. 1, 1978)

Jan. 1, 1979 - Oct. 31, 1979:

Post-doctoral: Kazushi Sugawara
Research Aide: Claire Yates

Advanced Degrees:

Connie M. Cooper received the M.S. degree in Physics in May, 1977.

It is anticipated that she will receive the Ph.D. in Physics in May, 1980.

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## REPORT DOCUMENTATION PAGE

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The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

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Ion implantation, conversion of insulating ferroelectrics to semiconductors

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The object of this work was to study ion implantation in perovskite ferroelectrics and to investigate the conductive behavior of implanted layers. Implantation experiments were carried out on strontium titanate, barium titanate (single crystal and ceramic), titanium dioxide (rutile), lithium niobate, and lithium tantalate. Ion beams attempted were $H^{(+)}$, $B^{(+)}$, $C^{(+)}$, $N^{(+)}$, $Fe^{(+)}$, $Ar^{(+)}$, $As^{(+)}$, $Ta^{(+)}$, and $Nb^{(++)}$. In general the most effective ion in producing conductivity was boron, $B^{(+)}$. Significant conductivity was measured in the

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substrates above, except for single crystals of barium titanate and lithium tantalate.

sq. cm

Boron implanted in strontium titanate and subsequently annealed resulted in highly conductive layers, whose sheet resistance could be between 100 and 100,000 ohm ohm per square. The charge carrier mobility in this system was 5 $cm^2$/volt sec at room temperature, increasing to 100 $cm^2$/volt sec at 77 K. Implantation doses were $10^{16}$ to $10^{17}$ ions/$cm^2$. The implantation depth, as revealed by chemical stripping experiments, was about 500 nm. A conductive anomaly was measured in some samples at 105 K, the cubic-tetragonal transition temperature.

sq. cm

Conductive layers were created on lithium niobate by either boron or iron implantation, the latter being more effective. The minimum sheet resistance, measured for an iron dose of $10^{17}$ ions/$cm^2$, was about $10^4$ ions/square.

The implantation of boron in rutile caused conductive layers with a room temperature sheet resistance of about 5,000 ohms/square, increasing to $10^5$ ohms/square at 125 K. The Hall mobility varied between 1 and 8 $cm^2$/volt sec over this temperature range, but the temperature dependence did not correspond to that of bulk reduced rutile.

The semiconducting layers had Seebeck coefficients between 100 and 300 millivolts/degree K and showed diode characteristics with respect to metal electrodes. They represent novel semiconducting systems which may be useful in special applications.

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Abstract Submitted
for the March Meeting of the
American Physical Society

Physics and Astronomy
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Number 73

Suggested title of session in which paper should be placed
Ion Implantation and Laser Annealing

Depth Profiles of Electrical Conductivity in Implanted Strontium Titanate. ROBERT GERSON, EDWARD B. HALE, and PAUL HIMMELFARB, University of Missouri-Rolla, Rolla, MO 65401*. The implantation of boron into strontium titanate is known to result in a conductive layer at the surface of the crystal[1], but the layer thickness has not been previously measured. In this work a chemical stripping process was developed for stepwise removal of the layer, during a time period of the order of hours, using phosphoric acid at 55C. For samples which had boron ion doses between $5 \times 10^{16}$ and $10^{17}$ ions ions/cm$^2$, the stripping rate at the implanted surface was roughly one hundred times higher than that of the unimplanted crystal. The surface sheet resistance and the weight loss were determined after each stripping step. From these data the residual sheet resistance and the rate of weight loss were calculated as a function of depth from the implanted surface. The surface layer removal to double the sheet resistivity was found to be about 500 nm for 100 kV ions and 250 nm for 50 kV ions. These data are indicative of the implantation depth.

*Supported by the Army Research Office.

1) Connie M. Cooper, P. S. Nayar, Edward B. Hale, and Robert Gerson, J. Appl. Phys. 50, 2826 (1979).

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Prefer Standard Session